U.S. Patent Application

of

TIMOTHY J. HENLY

for

EXTREMELY STABLE DIESEL FUEL COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to diesel fuel compositions that are extremely stable against thermal degradation, sedimentation, and discoloration. The diesel fuel compositions of the present invention have been designed to be void or essentially void of certain heteroatomic compounds often present in diesel fuel and which have been discovered to cause the thermal degradation in the presence of nitrate-based cetane improver additives.

BACKGROUND OF THE INVENTION

The benefits of operating a diesel engine on a diesel fuel treated with a nitrate-based cetane improver are well known: improved cold starting, less combustion noise, smoother engine operation and reduced toxic pollutant emissions. It is known that diesel fuels containing nitrate-containing cetane improvers often exhibit instability in the form of discoloration and sedimentation when heated to high temperatures (>120°C). It is also known that organic nitrate cetane improvers (e.g. 2-ethylhexyl nitrate, commercially available from Ethyl Corporation as HiTEC® 4103 cetane improver, also known as DII-3) can worsen diesel fuel discoloration and sedimentation in the 150°C pad stability test (ASTM D6468). The reasons for this phenomenon, however, have never been satisfactorily explained and several studies carried out over the years have failed to establish a correlation between any of a fuel's physical and chemical characteristics and its thermal stability. It has been widely observed that severely hydrotreated fuels are, in general, less susceptible to thermal degradation than conventionally refined fuels. Severe hydrotreatment reduces the amounts of heteroatomic species (i.e., compounds containing oxygen, nitrogen and/or sulfur atoms) in diesel fuel. Additionally, many published studies have implicated heteroatomic compounds in diesel fuel sedimentation at relatively low temperatures (below about 100°C). These results imply that heteroatomic compounds may be responsible for high-temperature

instability. None of these studies, however, addresses the issue of high-temperature diesel fuel instability in the presence of additives such as cetane improvers.

Several diesel fuels containing low amounts of total sulfur and/or nitrogen have been described. U.S. Patent No. 6,150,575 shows low sulfur diesel fuels; U.S. Patent No. 5,807,413 shows very low sulfur content and nitrogen content diesel fuels; U.S. Patent No. 5,792,339 shows low sulfur content and higher nitrogen content diesel fuels; U.S. Patent No. 5,389,111 and 5,389,112 show low sulfur content diesel fuels; EP 457589 shows a low sulfur content diesel fuel; and WO 00/12654 shows a very low sulfur content and nitrogen content diesel fuel. In all of these cases,the amounts of sulfur and nitrogen are considered only as bulk properties of the fuel; differences between chemical types of heteroatomic compounds are not taken into account. We have discovered that different types of heteroatomic molecules have different effects on a fuel's high-temperature stability in the presence of nitrate-based cetane improvers.

In the patents and patent applications involving ultralow-sulfur content diesel fuels (i.e., fuels with less than about 50 ppmw sulfur), the presence of nitrogen-containing additives such as nitrate-based cetane improvers is severely limited by the allowable or preferred total nitrogen content of the disclosed fuel compositions. Some of these patents and patent applications also require fuel compositions of limited aromatic content; however, low aromatic content is not required for this invention.

The patents, patent applications, and other documents recited herein are fully incorporated by reference.

Discoloration and sedimentation induced by nitrate-based cetane improvers can be undesirable to the consumer and can also interfere with common petroleum industry tests (e.g., ASTM D189, "Conradson Carbon Residue of Petroleum Products" and ASTM D524, "Ramsbottom Carbon Residue of Petroleum Products"). It is therefore desired to have a

diesel fuel composition which can demonstrate excellent thermal stability, i.e., lack of sedimentation and minimal discoloration upon heating to >120°C. It has been discovered that certain components in the diesel fuel are responsible for these undesired effects, and that by eliminating these certain components, an improved diesel fuel is produced.

SUMMARY OF THE INVENTION

A feature of the present invention is to provide a diesel fuel composition exhibiting improved ignition quality, which can demonstrate excellent thermal stability, i.e., lack of sedimentation and minimal discoloration when heated.

It has been discovered that certain heteroatomic compounds when present in diesel fuel containing nitrate-containing cetane improver cause severe discoloration and/or sedimentation when the fuel is heated.

It has also been discovered that the absence or removal of these certain heteroatomic compounds from diesel fuel containing, or to later contain, nitrate-containing cetane improver, significantly improves the fuel's thermal stability and minimizes discoloration and/or sedimentation.

Another feature of the present invention is to provide a diesel fuel composition containing a major amount of a hydrocarbon boiling in the middle distillate boiling range, and a minor amount of a nitrate-containing cetane improver, wherein the composition is free of, or essentially free of, certain heteroatomic compounds.

A further feature of the present invention is to provide a method of reducing the sedimentation and/or discoloration of a middle distillate fuel containing nitrate-based cetane improver.

Accordingly, the present invention relates to a diesel fuel composition containing a major amount of a hydrocarbon fuel boiling in the middle distillate boiling range, and a minor amount of a nitrate-containing cetane improver, wherein the composition is free of, or

essentially free of, one or more heteroatomic compounds selected from pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and/or indolines.

By "heteratomic compound" herein is meant one or more heteroatomic compounds selected from pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and/or indolines.

By "deleterious" heteroatomic compound herein is meant a heteroatomic compound that in a diesel fuel containing nitrated cetane improver causes discoloration and/or sedimentation of the diesel fuel upon heating of the fuel.

By "free of" in the present invention is meant a deleterious heteroatomic compound level generally undetectable in terms of adverse effect on color and sediment formation of the diesel fuel. This level is generally a level of less than about 2 ppm of deleterious heteroatomic compound in the finished diesel fuel. Similarly, by "removing all of" herein is meant a remaining level, if any, of deleterious heteratomic compound of less than about 2 ppm.

By "essentially free of" in the present invention is meant a level of less than about 5 ppm of heteroatomic compound in the finished diesel fuel. Similarly, by "removing essentially all of" herein is meant a remaining level, if any, of heteratomic compound of less than about 5 ppm.

By "nitrate-containing cetane improver" herein is meant chemical compounds that contain a nitrate group covalently bonded, ionically bonded, or generated *in situ*. Examples of nitrate-containing cetane improvers useful in the present invention include methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, *sec*-butyl nitrate, *tert*-butyl nitrate, amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, *n*-pentyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl

nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuranyl nitrate, tetraethyleneglycol dinitrate, isomers thereof, and mixtures thereof. A preferred nitrate-containing cetane improver in an embodiment of the present invention is 2-ethyl hexyl nitrate ("2-EH nitrate").

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

According to an embodiment of the present invention, an improved diesel fuel is prepared by combining a major amount of a middle distillate fuel, and a minor amount of a nitrate-based cetane improver, and removing before or after the addition of the nitrate-based cetane improver all or essentially all of one or more the following heteroatomic compounds: pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and/or indolines.

It has been discovered that middle distillate diesel fuel containing nitrate-based cetane improver has significantly improved thermal stability, i.e., reduced discoloration and reduced sedimentation, if the deleterious heteroatomic compounds of pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and/or indolines are removed or essentially removed from the fuel, relative to the comparable diesel fuel from which these heteroatomic compounds have not been removed. The aforementioned deleterious heteroatomic species may be removed by any method known to those skilled in the art, including hydrotreatment, selective adsorption, or oxidation.

The nitrate-based cetane improver can be present in the diesel fuel compositions of the present invention at a level of from about 100 ppm to about 10,000 ppm.

It has also been discovered that certain heteroatomic compounds do not have an

adverse or deleterious effect on sedimentation and discoloration of middle distillate fuel containing nitrate-based cetane improver. The heteroatomic compounds that do not have an adverse or deleterious effect on these properties of diesel fuel include anilines, pyridines, quinolines, amides, thiophenes, sulfoxides, phenols, carboxylic acids, nitriles, nitro compounds, aldehydes, esters, alcohols, peroxides, and carbazoles (see Table 1).

A benefit of this particular invention over the prior art is that certain species that are hard to remove from the diesel fuel by desulfurization and/or denitrogenation can be left in the fuel because they have been discovered herein to be innocuous in terms of thermal stability of the resulting diesel fuel. For example, most nitrogen compounds and thiophenes are more difficult to remove by hydrogenation than sulfides, mercaptans, etc. However, since most nitrogen compounds and thiophenes do not cause thermal instability of the diesel fuel, they can be left in the fuel at substantial savings to the refiner.

Compounds that cause thermal instability (degree of effect)	Compounds that do not cause thermal instability
Pyrroles (severe)	Anilines
Indoles (moderate to severe)	Pyridines
Indolines (moderate)	Quinolines
Sulfides (severe)	Amides
Disulfides (severe)	Carbazoles
Mercaptans (severe)	Thiophenes
Thioacids (severe)	Sulfoxides
Sulfonic acids (very severe)	Phenols
	Carboxylic acids
	Nitriles
	Nitro compounds
	Aldehydes
	Alcohols
	Esters
	Peroxides

Table 1. Summary of tendencies of heteroatomic compounds to cause thermal instability of diesel fuel containing 2-EH nitrate

Thus, in another embodiment of the present invention is provided a low sulfur D-2 (ASTM D975) diesel fuel having the following properties:

Cetane number, ASTM D613 35-60, and preferably 40-55

Cetane index, ASTM D4737 <60

Aromatics, total, wt. % ASTM D5186 <40

Polynuclear aromatics, wt. %, ASTM D2425 <11

Sulfur, ppmw, ASTM D2622-1 <50

Nitrogen, ppmw ASTM D4629 <1000 (from all sources)

Pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and indolines < 5 ppm total heteroatomic content. In a preferred embodiment, the amount of each of pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and indolines is no more than 5 ppm, and in a more preferred embodiment, no more than 2 ppm.

In addition, the present invention provides in another embodiment a diesel fuel meeting the requirements of ASTM D 975 for a low sulfur No. 2-D diesel and providing emission benefits at least equivalent to a diesel fuel as per Section 2282(g), Title 13, California Code of Regulations, said fuel containing from about 10 vol. % to about 30 vol. % aromatics and having (1) a Cetane number of at least 40 but less than 60, and preferably from 45 to 55; (2) a nitrogen content of no greater than 1000 ppmw; (3) a sulfur content of no greater than 50 ppmw; and (4) a total amount of nitrogen and sulfur from pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids and/or indolines of no more than 5 ppm, preferably no more than 2 ppm. In a preferred embodiment, the amount of each of pyrroles, indoles, sulfides, disulfides, mercaptans, thioacids, sulfonic acids, and indolines is no more than 5 ppm, and in a more preferred embodiment, no more than 2 ppm.

The following examples further illustrate aspects of the present invention but do not limit the present invention.

EXAMPLES:

An ultralow-sulfur diesel fuel (Fuel 9041), with inspection data as listed in Table 2, was separately treated with enough of each of the additives listed in Table 1 to deliver 350 ppm of oxygen, nitrogen, or sulfur. Fuel 9041 contained very low amounts of sulfur and nitrogen, but was in all other properties typical for a No. 2 diesel fuel. The base fuel with no added heteroatomic compound was very stable in the presence of 2-EH nitrate, ensuring that any instability observed in subsequent experiments arose from the introduced heteroatomic species. The heteroatomic compounds were selected as representative of compounds that might typically be expected to be found in a diesel fuel. Half of each fuel composition was treated with 2500 ppmv of 2-EH nitrate. The nitrate-free and nitrate-containing fuel compositions were subjected to 180-minute thermal stability testing at 150°C as described in pad stability test ASTM D6468.

Aromatics, vol. %	33.6
Olefins, vol. %	2.1
Saturates, vol. %	64.3
Specific gravity	0.850
T_{10}, °C	222
T_{50}, °C	271
T_{90}, °C	323
Sulfur, ppmw	7
Nitrogen, ppmw	27
Cetane number	44.2
Kinematic viscosity, cSt, 40°C	2.87

Table 2. Inspection data for Fuel 9041

In the thermal pad stability test ASTM D6468, the reflectance of light on a filter pad is measured and higher pad reflectances are desired as indicia that less sedimentation has occurred in the fuel.

Results from Thermal Stability Pad Test (ASTM D6468)

Oxygen-containing compound **w/o DII-3** **w/ DII-3**

None	98.7	97.3
Phenylacetaldehyde	99.6	99.7
Dimethylmalonate	99.5	99.6
p-Cresol	98.6	98.2
Lauric acid	98.6	96.1
2-Ethylhexanol	94.9	97.1
di-*t*-butyl peroxide	94.9	95.8
Benzoic acid	94.0	95.0
Sulfur-containing compound	**w/o DII-3**	**w/ DII-3**
None	98.7	97.3
Thianaphthene	97.5	97.2
Dimethyl sulfoxide	96.5	97.2
Di-*t*-butyl sulfide	48.7	3.7
4-methylbenzenethiol	24.8	12.0
1-octanethiol	12.6	3.3
Di-*t*-butyl disulfide	7.4	2.5
Thiobenzoic acid	7.3	1.8
p-Toluenesulfonic acid	3.8	1.0
Nitrogen-containing compound	**w/o DII-3**	**w/ DII-3**
None	98.7	97.3
N,N-dimethylaniline	98.6	96.0
3,5-lutidine	98.5	97.1
2,5-dimethylaniline	98.1	98.3
3-nitrotoluene	98.0	94.4
Quinaldine	97.4	97.5

2,4,6-collidine	97.1	96.9
Benzonitrile	94.9	97.9
2-pyrrolidinone	91.6	97.7
Indole	84.8	91.5
2-methylindole	79.6	48.6
Indoline	62.3	65.7
2,5-dimethylpyrrole	7.0	3.1

A number of conclusions can be drawn from these results. First, oxygen-containing compounds, even moderately strong carboxylic acids, have no adverse effect on the diesel fuel containing 2-EH nitrate cetane improver when the fuel was subjected to thermal stressing. With the exception of pyrroles and indoles, the same is true for the nitrogenous compounds investigated. In contrast, most of the sulfur-containing species studied had a strongly detrimental effect on the thermal stability of diesel fuel containing 2-EH nitrate.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims. This invention is susceptible to considerable variation in its practice. Accordingly, this invention is not limited to the specific exemplifications set forth hereinabove. Rather, this invention is within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

The patentee does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope

of the claims, they are considered to be part of the invention under the doctrine of equivalents.